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Trace Metals and the Environment: Studying the Behaviour of Iceland's Glacially Sourced Trace Metals

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Abstract

Trace metal contamination in marine ecosystems is a problem for every trophic level, from zooplankton up to humans. The mobility and uptake availability of these metals depend on such environmental parameters as salinity, temperature, and pH, among others. To explore the effects of varying parameters on dissolved metal behaviour, I studied the Jökulsárlón glacial lagoon, into which the Breiðamerkurjökull glacier deposits trace metals from volcanic ash through glacial melt. In this study I develop and follow a sampling procedure to analyze trace metal concentrations in the lagoon, while additionally discussing the behaviour and impact of trace metals, focusing on cadmium, in such varying environmental parameters as would be found in the Jökulsárlón lagoon and surrounding marine ecosystems.

Introduction

Iceland is a volcanically active island in the north Atlantic,[1] and is roughly 10% covered by glaciers.[2] These two natural processes interact in many ways. Glaciers form as layer upon layer of ice collect on top of a large body of snow and ice, which then moves under its own weight. In Iceland, volcanic eruptions occasionally cover a layer of glacier ice with ash and other volcanic debris. These layers are then covered by the following season's snow and ice, and the process continues. This over time leads to a highly stratified, ash-mixed glacier.[2]

Consequently, when glaciers in Iceland melt and calve into their pro-glacial lakes, these layers of ash are deposited. Since volcanic ash often contains heavy earth metals, this deposition of ash in glacial lagoons is an interesting topic to study, especially how these inevitably trace-metal concentrated waters will affect local ecosystems.[3] Additionally, as the planet warms, the rate of glacier ice melting– thus the rate of ash deposition– will increase. Over time, this will lead to even higher elevated concentrations of trace metals collecting in coastal regions.

The Jökulsárlón glacier lagoon is no different. Fed by the Breiðamerkurjökull glacier flowing from the Vatnajokull ice cap, the lagoon measures around 8 km in length, and is expanding every day.[4] Jökulsárlón is directly connected to the Atlantic Ocean's coastal waterways through a 6 m deep narrow channel.[4] Each tidal cycle, fresh water exits from the lagoon and warm saline ocean water enters through this channel.[4] These waters mix through the depths of the lagoon, with the saline Atlantic water flowing all the way to the terminus of the glacier.[4] The surface water of the lagoon is thus a combination of ice melt, fresh water and Atlantic derived saltwater.

This mixture of water sources with different pH, temperature, and salinity measures makes for an interesting study location on the impact of aforementioned trace metals on ecosystems. Trace metals complex and adsorb very differently as these conditions vary.[5] As such, this environment would be an excellent indicator for observations regarding the behaviour of dissolved and particulate trace metals in coastal waters, where fresh water and glacial melt meet saline ocean water.

I set out to determine whether the distance to the mouth of the lagoon had any effect on trace metal concentrations, in order to discern whether or not trace metal introduction to a coastal ecosystems might be impactful. This data would corroborate or negate if a relationship between the two main water sources of the lagoon and trace metal concentrations exists.

In this paper I will explore both the effects that the varying environmental factors in Jökulsárlón have on trace metals and the effects that these trace metals, focusing on cadmium, have on the important coastal species most at risk of exposure.

Methods: Sampling

Samples were collected using 30 mL PETG square bottles with HDPE lids. These bottles and lids were put through an acid bath procedure for 25 hours in 10% HNO_3 with the help of Dr. Sean Scully and Eva Maria Ingvadottir at the University of Akureyri. Each bottle was individually rinsed twice after the bath with distilled water, then dried upside down and sealed.

Samples were collected just as low tide began throughout a two hour period. The samples were collected by kayak, along with GPS positioning, water pH and temperature. Sample bottles were rinsed once in the lagoon's water at their site, then immediately filled to the brim and capped. Six samples were taken at each of the six sites (A-F). These sites followed the environmental gradient shown below. After collection, the samples were stored in a cold dark place until their lab preparation.

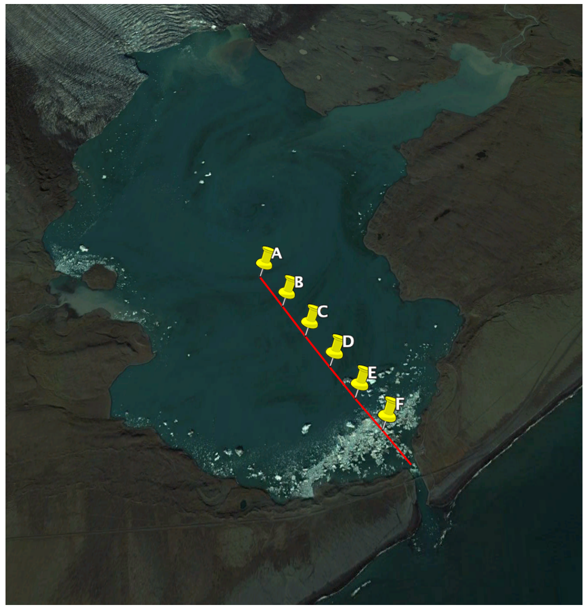

Figure 1: Planned sample sites A-F, with varying distance from the mouth of the lagoon. Image taken through Google Earth satellite imagery.

With the help of Dr. Sólveig Rósa Ólafsdóttir at the Marine and Freshwater Research Institute, a near-trace metal clean procedure was developed. Syringes were initially rinsed with a chelating agent, then deionized (DI) water, then acid, then DI water again. Between samples taken at the same site, the syringe and filter were rinsed with DI water. Between samples of discrete sites, the syringe was rinsed with DI water, then acid, then DI water, and the filter was replaced and rinsed with DI water. Each sample was filtered through 0.45μm Whatman filters using the syringe. Additional caution was taken to ensure that the samples did not touch the rubber in the syringe. Immediately after filtration, 60μL of 65% HNO_3 were added to each sample (0.2% by volume). Samples were shipped through the Icelandic Posturinn service and USPS.

Methods: Literature Analysis

My approach to the literature analysis section was to piece together a story connecting the South Iceland coastal ecosystem to environmental parameters which control trace metal concentrations. I used verified Icelandic databases, established ecological benchmarks, and peer-reviewed studies to connect these three topics.

Discussion

Trace metal data collection is tricky, to say the least. In order to follow a trace metal clean procedure, all equipment must at the very least be extensively acid bathed, and metal complexing detergent should be used liberally. Since laboratory availability was nonexistent near my sampling site, acid bath procedures took place hastily and with clean, but not trace metal clean, equipment. I was unable to use Milli-Q water for dilution of the acid, and the deionized water that I was able to use smelled of sulfur, a telling sign that it was not pure water and might have contaminants. Additionally, due to COVID regulations, my access to laboratory workplaces was very time restricted. I had only one day to prepare my samples for shipment, a day in which I was not able to follow full acid bathing and detergent soaking procedures.

Additionally, the lagoon itself poses a dilemma when sampling. The depth of the lagoon reaches past 250 m at some points, with much variation in temperature, pH, and salinity at different depths, as demonstrated in Figure 2. As such, sampling just the surface water does not reflect an accurate measure of properties of the lagoon as a whole.

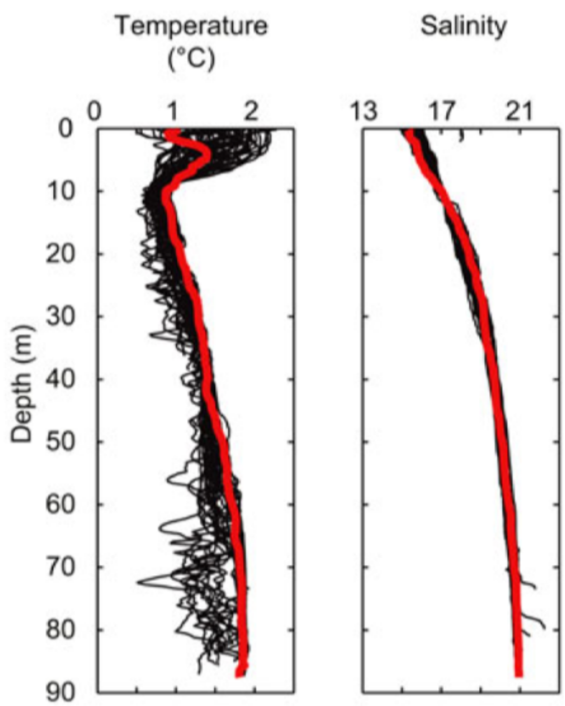

Figure 2: Vertical profile of temperature and salinity of Jökulsárlón.[4] To note are large surface variations in temperature and increasing trends in both measures as depth increases.

Finally, the deposition of ash in the lagoon is not a constant, measurable flow.[4] The main source of freshwater and ash from the glacier comes from subglacial discharge, which often emerges in large plumes all at once.[4] This is evident in satellite imagery (for example, in Figure 1), where large dark plumes can be seen in some areas and not others in the lagoon.

In conclusion, while the sampling methodology outlined and utilized here was the best possible process in terms of time-frame, accessibility, and equipment, it is inherently flawed and it would be irresponsible to consider the results of this study as reflective of the lagoon as a whole.

Additionally, due to the COVID-19 pandemic and the U.S. election involving a large increase in mail traffic, shipping both from Iceland and to the U.S. was drastically slowed during the time-frame of this project. While I was able to follow a tight schedule with regards to sampling, shipping preparation and shipping itself, my samples did not reach the laboratory in the U.S. where they were to be analyzed. This paper is therefore a combination of a field study and applied literature review analysis, with literature analysis composing most of the following.

Results: Sampling

The data we were able to collect were pH levels varying from 8.29 to 8.21 through the lagoon, and the qualitative observations of an incoming tide and weather conditions improving throughout sampling.

Results and Discussion: Literature Analysis

Different trace metals have varying effects on species and ecosystems alike. For this reason, in this section I discuss two key food web species present in the coast of Southern Iceland, then explore the environmental implications related to the heightened concentrations of important metals likely to be found in Jökulsárlón, focusing on cadmium. This section provides an unconventional combination of both the results and the discussion sections.

The food web in the Southern coast of Iceland is controlled mainly by high primary production, with capelin as a keystone species.[6] Capelin feeds almost entirely on euphausiids and copepods, of which the mesozooplankton *Calanus finmarchicus* is dominant.[6] Zooplankton are an important link between element transfer in the dissolved phase and its entry to the food web: 60-80% of dissolved Co, 50-60% of dissolved Cd, and 20% of dissolved Zn are taken up by zooplankton directly from the dissolved phase.[7] As such, I focus my analysis of trace metal effects on these two trophic levels. Table 1 displays the lowest test EC20 benchmarks for these levels with regards to the metals most likely to be deposited by volcanic ash.[3,8]

Table 1: EC20 results for marine animals. This table displays the highest tested concentration not causing a reduction of as much as 20% in the reproductive output of female test organisms.[8]

	EC20 Daphnids (ppm)	EC20 Fish (ppm)
Al	0.54	4.7
Cd	0.00075	0.0018
Co	0.0044	0.81
Cu	0.000205	0.005
Fe	0.016	-
Mn	1.1	1.27
Ni	0.045	0.062
Zn	-	0.047

As demonstrated by the data in Table 1, the concentration at which each trace metal is harmful is very different both for each trace metal and between the two trophic levels highlighted.[8] These benchmarks are often representative of the natural proportions of the concentrations of such metals, but volcanic ash deposition often disturbs these natural proportions. A study completed in 2015 at Jökulsárlón found the concentrations of many trace metals, displayed in Table 2.[9] These concentrations demonstrate the skewed proportions of trace metals due to the release of ash.[9]

Table 2: Concentrations of heavy trace metals in the Jökulsárlón glacial lagoon in 2015.[9]

	Al	Cd	Cu	Fe	Mn	Ni	Zn
Conc. (ppm)	0.132	0.00003	0.028	0.143	0.0167	0.0021	0.0025

These results are mostly promising for marine life within the lagoon, and for the waters outside of the lagoon. However, the heightened concentration of iron, above the EC20 benchmark for daphnia, poses a concern. Under certain circumstances, high concentrations of iron can result in a trophic mismatch event, in which an algal bloom throws the coastal ecosystem's nutrient availability out of balance.[3]

Another concern with trace metal deposition into ecosystems is bioaccumulation.[10] Since these metals are often deposited in the organs of marine animals and not cycled through their bodies, concentrations of metals increase up the food web.[10] Bioaccumulation through the marine food web is important, especially in Iceland, where the fishing industry holds an important role in both diet and economy. Trace metals accumulate from zooplankton to herring to capelin, the last of which finds its way onto dinner tables throughout the country and the world. While the found concentrations in the lagoon may be lower than established ecological benchmarks, it is important to understand the link between these concentrations and our own food systems, to understand that amplification of concentrations does indeed occur up the food web.[10]

Trace metal behaviour is also affected by the local properties in the water in which it is dissolved. As such, it is important to discuss that the lagoon is far from homogeneous. While warm, saline ocean waters flow northbound into the lagoon, fresh, cold glacial meltwater flows southbound into the lagoon, resulting in advection and diffusion between the two.[4] The warmer, saline ocean water is mostly sediment free, and tends to gather along the trenches at the bottom of the lagoon, before rising and mixing in.[4] The source of the freshwater comes from mostly subglacial discharge.[4] Subglacial discharge is laden with particulate matter, is completely salinity free, and is around 0°C.[4] As previously mentioned, these discharges tend to emerge in pulses, and can be observed through satellite imagery as visible plumes of dark sediment. The mixture of these very different water sources leads to high variations in important properties throughout the lagoon.[4]

Trace metals' dissolved concentrations depend highly on these properties– namely temperature, salinity and pH. As previously discussed, the Jökulsárlón lagoon has high variation in both temperature and salinity, making it an important stepping stone between freshwater glacial lagoons laden with trace metals and saline coastal waterways mostly free of them. By measuring adsorption rates –rates of accumulation of dissolved particles onto suspended particulate matter (SPM)– of different trace metals at different salinity levels, we can estimate the effect that the presence of saline water will have on the glacial lagoon. Figure 3 displays the results for a recent study which explored this relationship.

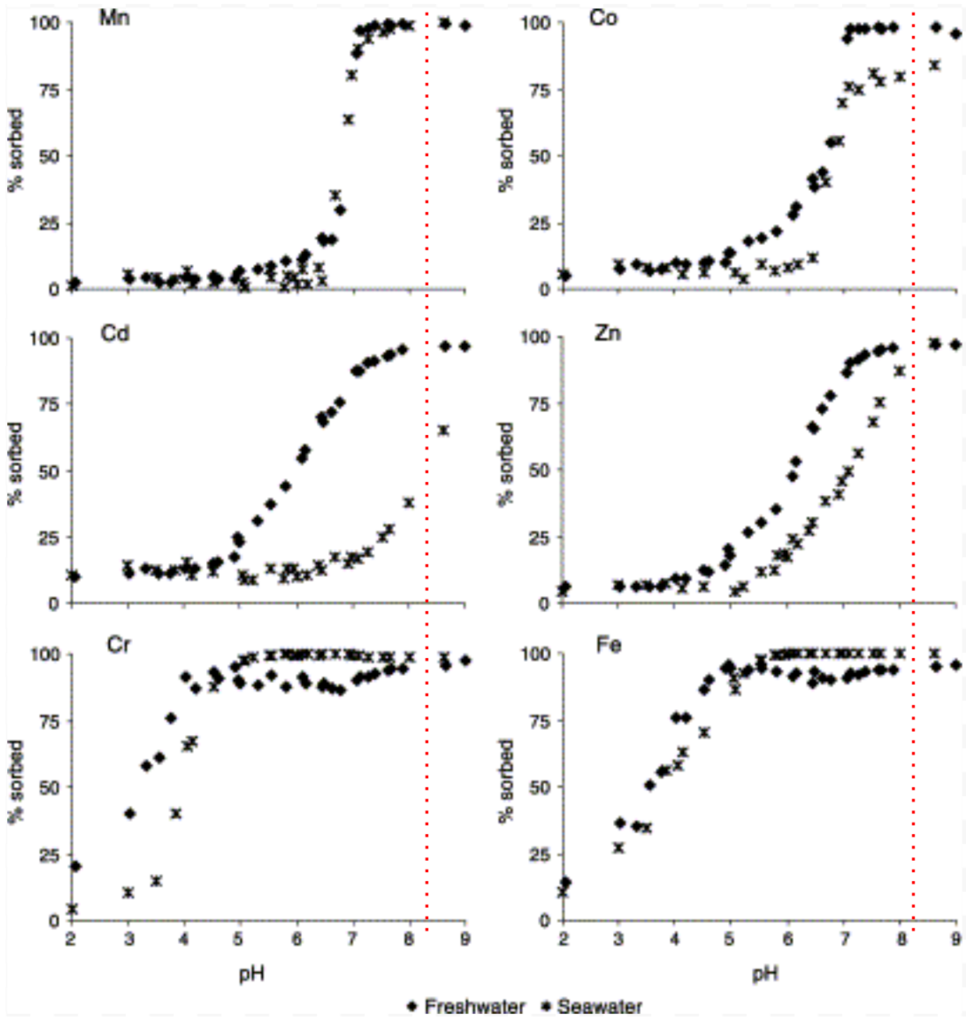

Figure 3: Relationship between trace metal concentrations and pH with fresh and saline water.[11] The dotted red line highlights a pH of 8.25, the measured pH level of surface waters of Jökulsárlón at the time of sampling.

The sigmoid curves observed here are characteristic of the interaction between dissolved metals and deprotonated sites on the surface of the SPM.[11] We could explore the reasons behind the differences in the slopes of these curves– broadly, metal-binding intensities, site densities, and reaction stoichiometries– but for our purposes, the differences between saline and freshwater adsorption is most important to compare. In that regard, since the measured pH in the lagoon was around 8.25 throughout my sampling, we will look closer at such rates for each metal.

Gathered from this study, both cobalt and cadmium show higher adsorption rates in freshwater than seawater at the lagoon's pH, while manganese and zinc rates are the same, and iron and chromium have slightly higher adsorption in seawater than freshwater.[11]

This means that adsorbed Co and Cd particles in the freshwater melt will have higher dissolution rates once they reach saline waters, while Mn and Zn will not change, and dissolved Fe and Cr will adsorbed out of the dissolved phase at higher rates.

Of most import is the increased rate of desorption of cadmium in saline water. Another study reporting on specifically cadmium's chemical response to increasing salinity found drastic changes in the concentration of dissolved cadmium before and after an increase in salinity.[12] Cadmium's mobility and thus availability for biological uptake increased significantly across four sample sites.[12] These studies clearly demonstrate the fact that an increase in the bioavailability and uptake of cadmium is directly related to higher rates of desorption of cadmium from SPM, which in turn is induced by an increase in salinity. This conclusion has interesting implications, as it suggests that the slightly higher quantity of suspended cadmium in some other glacial lagoons across Iceland,[9] once in contact with saline water, will desorb into the dissolved phase and therefore become more available for uptake by organisms.

Other studies have highlighted an increased mobility of trace metals from particles once contact is made with saline water. A study focusing on urban particles found increased mobility in Co, Cd, Zn, and Ni.[13] These four metals were found to have systematically increasing dissolved concentrations with increasing salinity, again with cadmium's mobility increasing more than the others.[13] Yet another study found increasing links in salinity and concentration of dissolved trace metals.[5] Figure 4 displays this study's results.

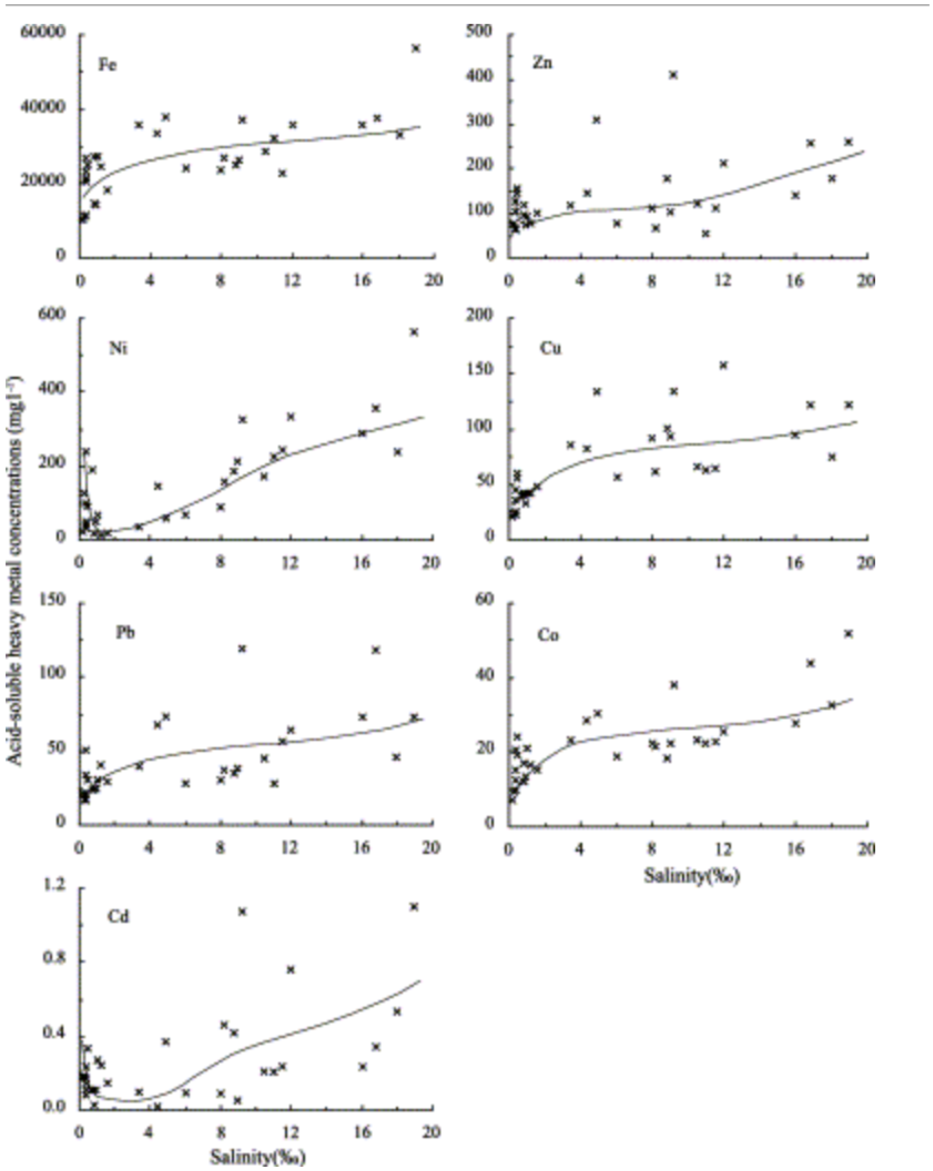

Figure 4: The relationship between the concentrations of trace metals with increasing salinities. Line of best fit data is included.[5]

Again, the most noticeably direct relationship between the two variables is apparent in cadmium concentrations– however, this study shows an increasing trend across the whole salinity range. All seven heavy metals studied here demonstrated increasing dissolved concentrations with increasing salinity.[5]

The differences between the results of these distinct studies can be explained by unmentioned environmental factors, such as temperature differences, metal supply, or biological factors within each body of water. However, it is important to note that with an increase of salinity, the behaviour of suspended trace metals certainly does change, and that in Iceland's glacial lagoons, salinity introduction would very likely result in a large desorption of suspended trace metals.[5]

While it is impactful to discuss the results of these studies, it is also important to understand the mechanisms which govern the increase of mobility of some trace metals in more saline waters. While many trace metals have ambiguous sources of dissolution, cadmium's saline water chemistry has been satisfactorily resolved.[5] Both laboratory experiments and field data corroborate that cadmium becomes desorbed from SPM in saline waters due to the formation of stable cadmium-chloride complexes.[5] These complexes form more readily with more chloride availability, which saline waters provide. Thus it would follow that in saline waters, desorption of cadmium would occur at greater rates than in fresh waters. Figure 5 depicts this process of complexing.

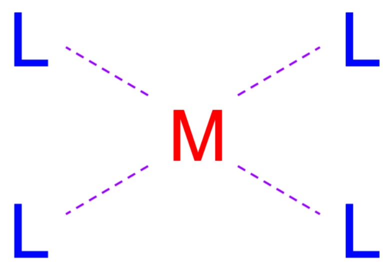

Figure 5: A metal (M) in a chelating complex with four ligands (L). Electrons are shared through coordinate covalent bonds. Figure created by ISP author.

The stable cadmium-chloride complex $[CdCl_4]^{2-}$ can be simplified into the complexing graphic in Figure 5. It is through the formation of this complex that cadmium is desorbed from the SPM and enters the dissolved phase.

Conclusions

The properties which govern the concentrations of dissolved trace metals in saline and fresh waters are complicated. However, we have identified the major processes that contribute most to these concentrations. By considering these processes when discussing concentrations measured in glacial lagoons throughout the southern coast of Iceland, we can predict the possibly dangerous effects that saltwater entry to glacial lagoons may induce. While climate change threatens the lives of glaciers and causes higher rates of melting, faster ash deposition will follow and larger glacial lagoons will form. It is inevitable that, if global warming continues at this scale, ash deposition in coastal saline waters will contaminate and influence marine ecosystems, from zooplankton up to human consumption.

Future studies should focus their attention on longer-span effects of faster glacial melt on the waters immediately outside of the lagoon, or on the range of elevated trace metal concentrations in these coastal waters. To fully grasp the environmental implications of these processes, we must understand the scope of its impact, and more broad, longer time-scale projects are the key to finding such data.

Ethics

As no animal or human subjects were involved, this project did not approach many ethical dilemmas. Sample collection was done by myself and a volunteer on our own time, with sterile nitrile gloves and acid cleaned equipment. All laboratory work was done with voluntary permission of representatives of their respective labs, and completed with proper protective equipment. Standard procedure disposal of acid and detergent solutions was carried out with supervision and care. No animals were harmed in this study, and no glacial ice was disturbed.

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